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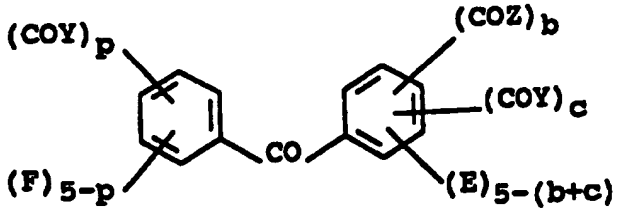

(I)

(57) Abstract

Benzophenone compounds of general formula (I) wherein: each Z independently represents an alkylene polyol moiety or a polyalkylene polyol moiety, wherein hydroxyl groups of the polyol moiety are optionally alkylated; each Y independently represents an alkylene polyol moiety or a polyalkylene polyol moiety, wherein hydroxyl groups of the polyol moiety are optionally alkylated; or an alkoxy group; each E is independently selected from hydrogen or halogen atoms and alkyl, acyl, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl, alkylsulphonyl, sulphonate, amido, alkylamido, alkoxycarbonyl, halocarbonyl and haloalkyl groups; each F is independently selected from hydrogen or halogen atoms and alkyl, acyl, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl, alkylsulphonyl, sulphonate, amido, alkylamido, alkoxycarbonyl, halocarbonyl and haloalkyl groups; b represents 1 to 5; c represents 0 to 4; and p represents 0 to 5 and processes for their preparation are described. Compounds of general formula (I) are useful as photoinitiators.

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BENZOPHENONE DERIVATIVES USEFUL AS PHOTOINITIATORS

This invention relates to novel benzophenone derivatives, to their preparation, to their use as photoinitiators in polymerisation processes, and to polymeric products cured using such photoinitiators.

Photoinitiated curing processes may use photoinitiators which generate photo-excited species, which react with the curing agents, commonly called synergists, to produce radicals which are thought to be the species responsible for the polymerisation reaction. Commonly the curing agents are aromatic tertiary amines. Commercial amine curing agents are ethyl-4-(N,N'-dimethylamino) benzoate (EDB) and 2-n-butoxyethyl 4-(dimethylamino) benzoate (BEDB).

Photoinitiators which are available, and suitable for use with amine curing agents, are thioxanthone initiators, in particular isopropylthioxanthone (ITX); anthroquinone initiators; and benzophenone initiators, in particular 2-methylbenzoylbenzoate (2-MBB).

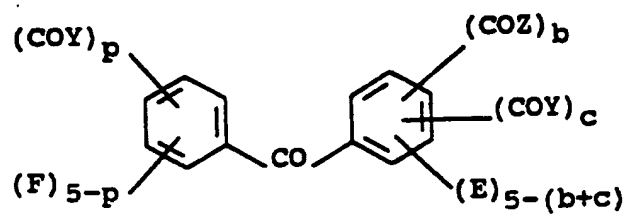
The invention concerns improvements in benzophenone initiators. Whilst benzophenone/amine curing systems have been extremely important they are now less favoured. In part this is because the benzophenone components, for example 2-MBB, tend to migrate relatively easily from the cured polymers, and taint adjacent materials. When the polymer is, for example, a film, and the adjacent materials are, for example, foodstuffs, this is very undesirable.

Japanese published patent application 6263814 (Toyo Ink) proposes photoinitiators obtained by reacting

dihydric polyol compounds with ortho-benzoylbenzoic acid. These are said to be of use in curable coating compositions said to have reduced odour, and to be free from deterioration from curability. However, in experiments we have found the di(benzoyl benzoate) compound of this type produced by reacting ortho-benzoylbenzoic acid with poly(ethylene glycol)$_{300}$ to migrate from a cured polymer at a relatively high rate.

We have discovered certain benzoylbenzoate derivatives which appear to have a surprisingly low propensity to migrate from a cured polymer.

In accordance with a first aspect of the present invention, there is provided a benzophenone compound of the general formula



(I)

wherein:

each Z independently represents an alkylene polyol moiety or a polyalkylene polyol moiety, wherein hydroxyl groups of the polyol moiety are optionally alkylated;

each Y independently represents an alkylene polyol moiety or a polyalkylene polyol moiety, wherein hydroxyl groups of the polyol moiety are optionally alkylated; or an alkoxy group;

each E is independently selected from hydrogen or halogen atoms and alkyl, acyl, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl,

alkylsulphonyl, sulphonate, amido, alkylamido, alkoxycarbonyl, halocarbonyl and haloalkyl groups;
each F is independently selected from hydrogen or halogen atoms and alkyl, acyl, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl, alkylsulphonyl, sulphonate, amido, alkylamido, alkoxycarbonyl, halocarbonyl and haloalkyl groups;
b represents 1 to 5;
c represents 0 to 4; and
p represents 0 to 5.

Suitably, b represents 1 or 2, preferably 1.

Suitably, c represents 0 or 1, preferably 0.

Suitably, each E represents a hydrogen atom.

Suitably, p represents 0 or 1.

Suitably, each F represents a hydrogen atom.

Suitably, one or each group Z includes at least two ether functionalities.

Suitably, the or each group Z independently represents an alkylene glycol or polyalkylene glycol moiety wherein hydroxyl groups of the moiety are optionally alkylated.

Suitably, the or each group Z represents an ethylene glycol or polyethylene glycol moiety, wherein hydroxyl groups of the moiety are optionally alkylated.

Suitably, one or preferably each, group Z represents a polyol moiety which is end-capped by an alkyl group.

Suitably, an alkyl group which end caps the group Z is a C_{1-4} alkyl group. Preferably, it is a methyl group.

Suitably, one or preferably, each group Z represents a polyol moiety wherein each hydroxyl group is alkylated.

Suitably, one or preferably each group Z is of the general formula $-O-(CH_2-CH_2-O)_e$-alkyl where e has a mean value of from 2 to 20, preferably 4 to 15, most preferably 6 to 13 and the alkyl group is suitably a C_{1-4} alkyl group, preferably methyl.

Preferably, a said group COZ is located in the 2- or 4-position, most preferably in the 4-position.

Suitably, one or each group Y includes at least two ether functionalities.

Suitably, each Y independently represents an alkylene glycol or polyalkylene glycol moiety, wherein hydroxyl groups of the moiety are optionally alkylated.

Suitably, Y represents an ethylene glycol or polyethylene glycol moiety, wherein hydroxyl groups of the moiety are optionally alkylated.

Suitably, one or preferably each, group Y represents a polyol moiety which is end-capped by an alkyl group.

Suitably, an alkyl group which end caps the group Y is a C_{1-4} alkyl group. Preferably, it is a methyl group.

Suitably, one or preferably, each group Y represents a polyol moiety wherein each hydroxyl group is alkylated.

Preferably, one or preferably each group Y is of the general formula $-O-(CH_2-CH_2-O)_e$-alkyl where e has a mean value of from 2 to 20, preferably 4 to 15, most preferably 6 to 13.

Preferably, a said group COY is located in the 2- or 4-position, most preferably in the 4-position.

In accordance with a second aspect of the present invention there is provided a process for the preparation of a compound of the general formula I, which comprises the esterification or transesterification of a precursor benzophenone compound to the compound of general formula I, with an appropriate optionally alkylated polyol compound having at least one hydroxyl group.

When p and c each represent 0, the preferred reaction is an esterification, using the appropriate benzoyl benzoic acid.

When p and/or c represents 1 and Y represents an alkylene polyol or polyalkylene polyol moiety, optionally end-capped by an alkyl group, the preferred reaction is a transesterification, preferably from the appropriate di(methoxycarbonyl) benzophenone compound.

When p and/or c represents 1 and Y represents an alkoxy group the favoured reaction is an esterification, using the appropriate precursor compound having one or more (as applicable) ester groups COY, where each Y represents an alkoxy group, and one group -COOH.

Commercially available xylene derivatives may be suitable reagents for the preparation of compounds of general formula I.

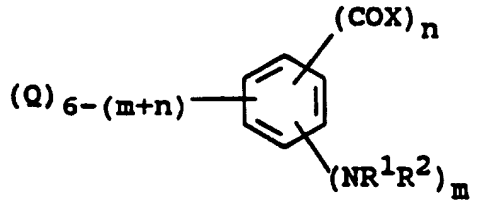
The esterification/transesterification may be carried out under standard conditions. The esterification reaction may be carried out in an organic solvent, for example toluene, at an elevated temperature, preferably under reflux, with removal of water during the reaction process. Suitably a catalyst is present. Suitable catalysts are tin (II) octanoate or an acid, suitably an organic acid, for example a sulphonic acid. The transesterification reaction may be carried out in an organic solvent, for example toluene, in the substantial absence of water, at an elevated temperature, preferably under reflux. Suitably a catalyst is present, preferably an alkyl titanate or an acid, suitably an organic acid, for example a sulphonic acid.

In accordance with a further aspect of the present invention there is provided a polymer curing composition, which may be in kit form, comprising a compound of general formula I as described above, together with a curing agent with which the compound of general formula I may react, when irradiated, to generate a polymerisation radical.

In accordance with a further aspect of the present invention there is provided a polymerisable composition comprising a polymerisable material suitably present in an amount from 80 to 97 wt. %, a curing agent suitably present in an amount from 14 to 2 wt. %, and a compound of the general formula I, suitably present in an amount from 6 to 1 wt. %.

In accordance with a further aspect of the present invention there is provided a polymeric composition derived from said polymerisable composition by photo-curing.

A suitable curing agent may, for example, be an aromatic amine compound, for example ethyl-4-(N,N-dimethylamino) benzoate (EDB) or 2-n-butoxyethyl 4-(dimethylamino) benzoate (BEDB). Preferably, however, it is a novel amine compound of the type defined in our co-filed patent application entitled "Novel Amine Curing Agents", the contents of which are incorporated herein by reference. Thus, such a compound is of the general formula



(II)

wherein:
each R^1 independently represents an alkyl group;
each R^2 independently represents an alkyl group;
each group X independently represents a polyalkylene polyol moiety wherein hydroxyl groups of the polyol moiety are optionally alkylated;
n and m independently represent 1, 2 or 3; and
each Q is independently selected from hydrogen or halogen atoms, and alkyl, acyl, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl, alkylsulphonyl, sulphonate, amido, alkylamido, alkoxycarbonyl, halocarbonyl and haloalkyl groups.

Suitably, n and m independently represent 1 or 2, preferably 1.

Suitably, each Q represents a hydrogen atom.

Suitably, each R^1 represents the same alkyl group.

Suitably, each R^1 represents a C_{1-4} alkyl group, preferably methyl.

Suitably, each R^2 represents the same alkyl group.

Suitably, each R^2 represents a C_{1-4} alkyl group, preferably methyl.

Suitably, one or each group X includes at least two ether functionalities.

Suitably, each X independently represents a polyalkylene glycol moiety, wherein hydroxyl groups of the moiety are optionally alkylated.

Suitably, each X represents a polyethylene glycol moiety, wherein hydroxyl groups of the moiety are optionally alkylated.

Suitably, one or preferably each, group X represents a polyol moiety which is end-capped by an alkyl group.

Suitably, the alkyl group which end caps the group X is a C_{1-4} alkyl group. Preferably, it is a methyl group.

Preferably, one or preferably each group X represents a polyol moiety wherein each hydroxyl group is alkylated.

Preferably, one or each group X is of the general formula $-O-(CH_2-CH_2-O)_z$-alkyl where z has a mean value of from 2 to 20, preferably 4 to 15, most preferably 6 to 13 and the alkyl group is suitably a C_{1-4} alkyl group, preferably methyl.

Preferably, at least one said group COX is located para to a said dialkylamine group. Where n = m = 1, preferably the group COX is located para to the dialkylamine group.

Compounds of the general formula II may be prepared by alkylation of a corresponding primary amine compound (in which R_1 = R_2 = hydrogen). This may be carried out by reductive alkylation, using the appropriate alkanal. Such a reaction can be carried out in a hydrogenator, at elevated temperature and pressure, and in the presence of hydrogen. The corresponding primary amine compound can itself be prepared by similar hydrogenation, from the corresponding nitro compound. The nitro compound may be easily prepared by reaction of the appropriate nitrobenzoic acid with the appropriate alkyl end-capped alkylene glycol compound, retaining a single hydroxyl group. Alternatively, the appropriate nitrobenzoic acid chloride may be employed, suitably with a base, for example an amine base, suitably triethylamine.

Alternatively, the compounds of the general formula II may be prepared by esterification of the appropriate dialkylamine benzoyl chloride compound, with the appropriate optionally alkylated polyol compound, having at least one hydroxyl group. This reaction suitably takes place in the presence of a base, for example an amine base, for example triethylamine. This reaction suitably takes place at a temperature in the range -20°C to 40°C, preferably 0°C to ambient temperature. The benzoyl chloride reactant may be prepared by the reaction of thionyl chloride with the corresponding benzoic acid, suitably at ambient temperature.

A suitable polymerisable material is any material whose polymerisation can be initiated by an amine radical. Preferably the polymerisation is applied to acrylate systems where the polymerisable material (monomer) may, for example be 1,6-hexanediol diacrylate (HDDA), 2-hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA) and methyl methacrylate (MMA).

The polymerisable materials may be suitable for surface/coating/film applications. They may be formulated with other components, including inks, for printing applications.

The invention will now be further described, by way of example.

Preparation of photoinitiators of the invention

Compound 1: 4-Benzoylbenzoyl poly(ethylene glycol)$_{350}$ monomethylether

2.1 g of poly(ethylene glycol)$_{350}$ mono methyl ether, 1 g of 4-benzoylbenzoic acid and 1 g of p-toluene sulphonic acid were refluxed with 100 ml of toluene until all water present had been driven over. Catalytic amounts of tin (II) octanoate were added and the mixture refluxed for 10 hours. After removal of the toluene, washing with sodium carbonate (to neutralise any free acid present) and drying under vacuum, a brown liquid was obtained (which became extremely viscous on standing). The product structure was confirmed by 100 MHz proton NMR, the results being as follows:

methyl ether 3.45 ppm singlet (3H)
ethylene protons 3.75 ppm singlet (~30H)
aromatic proton 7.60-8.50 ppm multiplet (9H)

Compound 2: Di-[poly(ethylene glycol)$_{350}$ monomethylether] benzophenone-4,4'-dicarboxylate

The first step was to prepare 4,4'-dimethyl benzophenone. To do this, 25 ml of p-toluoyl chloride was added slowly to a stirred mixture of 30 g of anhydrous aluminium trichloride and 115 ml of dry toluene. The resulting solution was refluxed for 6 hours before the product was isolated by addition of the reaction solution to a solution of 200 ml water and 100 ml conc. HCl. The resulting red solid was distilled (short path) at 141°C at 4 mm Hg. The distillate solidified on cooling to a white solid.

Melting point: = 90-92°C

Elemental analysis: $C_{15}H_{14}O$

requires % C = 85.68, H = 6.71

found % C = 85.66, H = 6.44

100 MHz proton NMR: solvent = CD_2Cl_2; aromatic protons 7-8 ppm AA^1BB^1 system (8H); methyl protons 2.4 ppm (6H).

The 4,4'-dimethyl benzophenone was then oxidised to the corresponding dicarboxylic acid. A solution of glacial acetic acid and the 4,4'-dimethyl benzophenone was added to a solution of aq. acetic acid 80 % v/v and chromium trioxide and stirred at ambient temperature for 24 hours. The addition of water facilitated a pale green precipitate. Isolation and H^1 NMR/elemental analysis showed partial oxidation. The reaction was driven to completion by refluxing, at 65°C, for 24 hours.

Elemental analysis: $C_{15}H_{10}O_5$

requires % C = 66.67, H = 3.74

found % C = 66.71, H = 3.65

60 MHz H^1 NMR aromatic protons exhibiting an AA^1BB^1 splitting system 8-8.5 ppm.

% Yield = 67.43%

FTIR exhibited a large -OH stretch (persisted after drying product in vacuum oven at 40°C for 48 hours).

The dicarboxylic acid compound was esterified to form the dimethyl ester. The esterification was achieved by refluxing in methanol and an acid for 24 hours. The crude product was taken into THF and washed with water to remove free acid. Recrystallisation was from dry ethanol. Characterisation was by H^1 NMR which gave the AA^1BB^1 aromatic splitting pattern (8.20-8.70 ppm) and a singlet assigned to the methyl protons (4.20 ppm). Integration was in the ratio 4 : 3. FTIR exhibited no -OH stretch after drying.

Elemental analysis:

requires % C = 68.45, H = 4.73
found % C = 68.67, H = 4.54

Finally, the dimethyl ester was transesterified to form the title compound. 2.5 g Dimethyl ester, 6.25 g poly(ethylene glycol)$_{350}$ monomethylether and 500 ml of dry toluene was refluxed in a Dean and Stark apparatus for 1 hour. 0.25 g of Tilcom [Trade Mark - $Ti(OPr)_2(OBu)_2$] was injected and refluxing at 100°C was continued for 4 hours. The methanol side product was removed using a fractionating column and the reaction was driven to completion by refluxing for a further 2.5 hours. Removal of the catalyst was achieved by addition of 2 ml of water to the vigorously stirred, cooled solution and filtration of the resulting precipitate of titanium oxide. The surplus water was removed by returning the toluene solution back to the Dean and Stark apparatus for 1 hour. Removal of the solvent produced a viscous, light brown liquid (yield c. 2 g).

Analysis:
60 MHz H^1 NMR;
methyl ether 3.45 ppm singlet (6H)
ethylene protons 3.75 ppm singlet (~58H)
aromatic protons 7.95-8.50 ppm AA^1BB^1 (8H)
HPLC; flow rate 1 ml/min, 254 nm, 20 micro litre sample loop, a 50/50 acetonitrile water mobile phase. The resulting trace showed two distinct groups of peaks, attributed to the mono and di-substituted PEG esters.

Compound 3: 2-Benzoylbenzoyl poly(ethylene glycol)$_{350}$ monomethylether

This compound was prepared by transesterification of 2-methyl benzoylbenzoate with poly(ethylene glycol)$_{350}$ monomethylether, in accordance with the method described with reference to Compound 2. The product structure was confirmed by 100 MHz proton NMR, the results being as follows:
methyl ether 3.75 ppm singlet (3H)
ethylene protons 3.65 ppm singlet (~30H)
aromatic protons 7.20-7.80 ppm multiplet (9H)

Comparison compounds

Compound C1: Di-[2-(benzoylbenzoyl ether)] poly(ethylene glycol)$_{300}$

This compound was prepared by transesterification of 2-methylbenzoyl benzoate with poly(ethylene glycol)$_{300}$, in accordance with the method described with reference to Compound 2.

Compound C2: 2-Methylbenzoyl benzoate

This compound was the commercial product SPEEDCURE MBB obtainable from Lambson Fine Chemicals Limited, of Castleford, U.K.

Compound C3: 4-Methyl benzoyl benzoate

This was prepared by standard esterification from 4-benzoylbenzoic acid and methanol, in the presence of concentrated sulphuric acid. The product was confirmed by NMR. mp 103-105°C.

Amine Curing Agents

As described below, the standard compound N-methyldiethanolamine (NMDA) was used in tests. However also used was a novel compound, 4-N,N'-dimethylaminobenzoyl poly(ethylene glycol)$_{350}$ monomethylether. This was prepared as follows.

To a 25 ml round bottom flask equipped with a 50 ml dropping funnel was added triethylamine (ex. Aldrich) (1.22 g, 1.1 mol equiv.). Poly(ethylene glycol) 350 monomethyl ether (ex. Fluka) (3.38 g, 0.01 mol) was then added. The mixture was dissolved in dry THF (20 ml). The flask was then placed in an ice bath and cooled to 0°C.

4-Dimethylamino benzoyl chloride (2.00 g, 0.01 mol) was also dissolved in dry THF (20 ml). This solution was placed in the dropping funnel, and added dropwise to the stirred cooled solution below. After the final addition of the acid chloride the solution was allowed to stir for 17 hours at ambient temperature.

The reaction was completed by removing the triethylamine hydrochloride by filtration, and the remaining solvent under reduced pressure. The residue that was left was redissolved in chloroform (50 ml) and washed with brine (15 ml). The organic layer was then removed and dried with sodium sulphate, filtered and the chloroform removed under reduced pressure. This yielded the novel amine compound as a yellow/brown semi-solid, more liquid than solid.

Data

Yield: 3.21 g

NMR ^1H (100 MHz, $CDCl_3$/TMS) δ (ppm): 6.5-7.9 (m,Ar,4H); 3.6 (s,PEG,manyH[~28]; 3.3 (s,OMe,3H); 3.0 (Me_2N-,6H).

IR (KBr) ν cm^{-1}: 2800-2960 (C-H); 1700 (C-O); 1620 (C=O); 770 (Ar).

$C_{24}H_{41}O_9N$

Microanalysis: Requires C: 59.13% H: 8.42% N: 2.87%
Found C: 57.81% H: 8.77% N: 2.35%

Homogeneity point: 50-60°C.

Extinction coefficient: 215600 @ 310.8 nm

Note on microanalysis

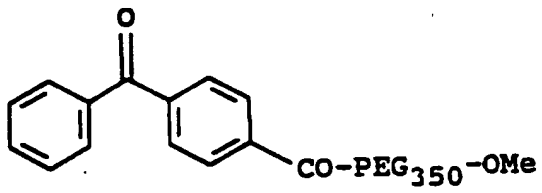
It has been noted that the microanalysis (CHN) results on all compounds containing polyethylene glycol (PEG) are not as accurate as desired. This is not due to impurities in the compounds, but to the fact that PEG compounds contain average chain lengths. For example, a PEG compound of average molecular weight 350 contains chains that vary in length between 2 and 12 ethylene glycol units. In order to calculate the percentage of carbon and hydrogen present in the chain it was necessary to determine the average number of units present. The method of calculating this is shown below.

PEG chain = 350
Repeating unit ($-OCH_2CH_2O-$) = 44.053
Mono methyl ether (OMe) = 31.034
350 - 31.034 = 318.966
318.966 divided by 44.053 = 7.24
= ~7 repeating units

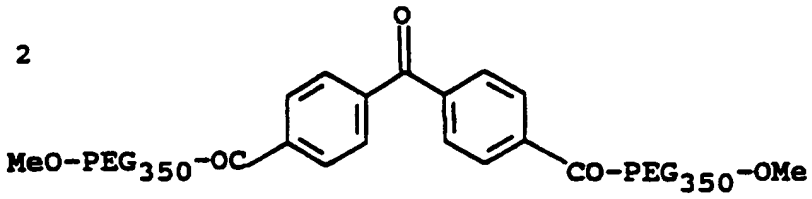
Therefore, one can assess the number of carbon, hydrogen and oxygen atoms in the chain and it is also possible to calculate the overall number of individual carbon, hydrogen and oxygen atoms and hence the overall percentage composition.

Summary of Compounds

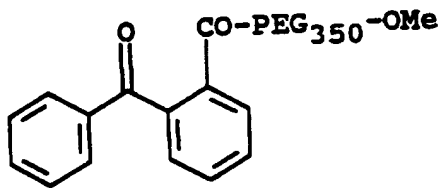
Compound 1



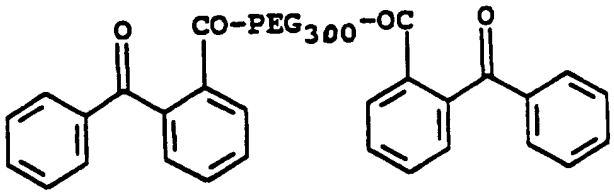
Compound 2



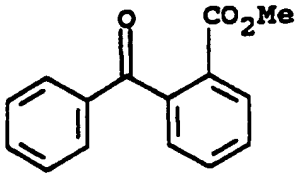
Compound 3



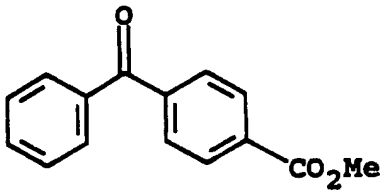
Compound C1



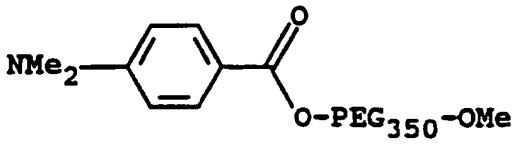
Compound C2



Compound C3



Compound A



Effectiveness of Compounds as Curing Agents

For the purpose of these tests, unless otherwise stated, the standard pre-polymer mixture was as follows:

1-6 hexanediol Diacrylate (monomer) : 93 wt %
amine curing agent : 5 wt %
photoinitiator : 2 wt %.

It was found that all of the compounds 1-3 and comparison compounds C1-C3 above, dissolved into the prepolymer mixtures.

Curing was by a medium pressure UV lamp. The results presented below relate to the determination of whether the polymer cures and if so, how quickly, and to the propensity of the photoinitiators to migrate from a polymer film after curing. The two methods employed to address these aspects were Real Time Infra Red (RT-IR) and High Pressure Liquid Chromography (HPLC).

Methods of Data Acquisition

RT-IR analysis of the rate of cure of each of the pre polymer mixtures

The use of RT-IR allows the rate of cure of each of the samples to be analysed. This method allows an infra-red spectrum to be taken, then a frequency is chosen, one at which the transmittance would change during polymerisation. Commonly used is the acrylate stretch at 810 cm^{-1}, the acrylate double bonds disappearing during curing. Using the time drive facility, it allows infra-red analysis while the sample is being irradiated with a medium pressure UV lamp, thus allowing the increase in

transmittance to be monitored. This gives an indication of the rate of polymerisation. A second spectrum was run. This showed the final position of the acrylate stretch.

Two RT-IR's were run on each pre-polymer mixture. The samples were prepared as follows. A drop of each pre-polymer mixture was placed between two polyethylene sheets in the centre of a polyether spacer of 25 μm. This was to ensure that all the films were of the same thickness. This sandwiched sample was then placed between two NaCl plates, which in turn were placed in a holder unit. This entire unit was then placed into the infra-red machine and the spectrum run.

HPLC method used for analysing the propensity of the initiators to migrate

The method for testing the propensity of the initiators to migrate was the same throughout.

The migratable initiator content of each film was analysed as follows. Initially a drop of the pre-polymer mixture was placed on a piece of satinised paper. This was then evenly spread over the surface using a "K" bar which gave a film thickness of between 50-60 μm.

For each of the initiators samples of film were taken after various passes of the Colordry unit (i.e., the UV lamp), as specified below in the tables.

The Colordry unit contains a medium pressure mercury lamp. The samples are placed on a moving belt (in these trials this was set at 24 metres/minute). It was important to ensure two main factors during this stage of the trial. Firstly, that all the samples taken, of

satinised paper and film, were of the same size. It was for this reason that a metal template was made that gave samples of 21 x 28 mm. Secondly, that the curing of the film was as unaffected by oxygen inhibition as possible. This was ensured by placing the paper and uncured film in a cell with a quartz window. This cell was then evacuated with nitrogen and sealed. Only then was the sample passed through the Colordry unit.

The 21 x 28 mm samples of each pre-polymer mixture were then placed in individual 7 ml sample vials. To each vial was added 5 ml of a de-gassed acetonitrile/water 50/50 mix, enough to immerse each sample. The vials were then placed in a dark cupboard for 20 hours. After this time the vials were removed and the sample extracted from each vial. All that was left in each vial was the solvent containing the migratables that had leached out from the film in the 20 hour period.

Methods of Data Analysis

RT-IR analysis of the rate of cure of each of the pre polymer mixtures

For each sample three spectra were run, to allow an average to be taken. Each spectrum had a decay curve which represents the rate of polymerisation. The steeper the gradient of the curve, the faster the rate. The angle of the gradient was measured and this could then be used to compare the rate of polymerisation achieved by different curing agents.

HPLC method used for analysing the migration of initiators from films

These samples were then prepared for HPLC analysis by filtering each one using Sartorus Millistart 0.45 μm disposable filters. This was to ensure that there were no solid contaminants that would damage the HPLC column.

Chromatographs of the initiator components for each of the films were run prior to the trials. This was to ensure that firstly the elution time was known and, secondly, to determine whether the respective initiator components had any characteristic shaped peaks.

After filtration each sample was injected on to the HPLC column. Each sample was run in acetonitrile/water 50/50 mixture. The data from each run was then used to analyse the migratable content of each film.

On the chromatogram for the solution containing migrated initiator compound, the area under each of the relevant peaks was noted.

It was assumed that the contents of the solution that had contained the film that had not passed the UV lamp, contained 100% migratable initiator compound, because the pre-polymer mixture was not irradiated. The values for the areas under the peaks from the solutions that had contained films that had passed the UV lamp could then be correlated respectively to the 100% migration value of the uncured solution.

Test set 1

In the first tests migration of the initiators from the cured films were studied. The curing agent was N-methyldiethanolamine (NMDA).

Table 1

Percentage migration of initiator after stated number of passes under UV source

No. of passes of UV source	Compound 1	Compound 2	Compound C1	Compound C2	Compound C3
0	100	100	100	100	100
2	20.24	86.12	62.1	47.29	69.31
4	15.79	57.07	53.37	55.23	52.83
8	14.89	32.87	51.07	29.73	55.07

It will be seen from Table 1, that compound 1 demonstrates a greatly reduced % of migration, and that even after 2 passes, the % migration is very low, indicating a high rate of polymerisation. Compound 2 is not so effective as compound 1 but nevertheless the % migration after 8 passes is similar to that of the commercial product, compound C2. Compound 2 unexpectedly achieves significantly better properties after 8 passes than compound C1, which is of the type disclosed in JP 6263814. A further significant aspect of the results is that, whereas compound C3, the 4-methyl ester, has poorer migration properties than compound C2, the corresponding 2-methyl ester, this pattern is not reproduced in the analogous PEG ester, where it is the 4-ester, compound 1, which has the better migration properties than the 2-ester, compound 2.

Test set 2

Further tests were carried out to explore further the use of compounds of the present invention as photoinitiators; and to assess their possible use with end-capped PEG esters of dialkylamino benzoic acids, the novel compounds of the co-filed application mentioned above, those PEG esters themselves having very good self-migration properties.

A) Migration studies as described above were carried out to assess the degree of migration when the curing agent was compound A described above (5 wt %), in comparison with NMDA (5 wt %). The photoinitiator was compound 1 (2 wt %) and the monomer HDDA (93 wt %).

Compound A was found to be fully compatible with the prepolymer formulation. The results are set out in Table 2 below.

Table 2

Percentage Migration of initiator compound 1 after stated number of passes under UV source, using alternative amine curing agents

No. of passes of UV source	0	2	3	4	5	7	8	9
Compound A	100	63.97	37.97	21.6	9.13	14.18	-	9.25
NMDA	100	20.25	-	15.79	-	-	14.89	-

It is seen that in a well cured film the PEG-substituted aromatic curing compound A agent makes little difference to the % migration of the PEG-modified photoinitiator compound 1. Therefore a formulation combining a low migration initiator and the novel low migration curing agent is possible.

B) The degree of migration from UV cured films of compound 2 was assessed, in comparison with compound 1. Due to the favourable results obtained when curing with compound A, this was used as the curing agent in these tests. The results are set out in Table 3 below.

Table 3

% Migration of compound 1 and 2

No. of passes of UV source	0	2	6	8
Compound 1	100	51.1	42.81	39.87
Compound 2	100	30.1	32.53	28.76

It can be seen that compound 2 yields a lower degree of migration than compound 1. It should be noted that these results are not properly comparable to the results A) above, due to the replacement of the curing belt.

C) Studies of the percentage cure of films using a range of curing systems

Although the novel PEG-substituted photoinitiators and curing agents have comparatively low migration from cured films, it was also necessary to test their efficiency in polymerising HDDA. This was assessed using FTIR as described above.

Curing Agent 5%, photoinitiator 2%, HDDA 93%

a) Ethyl-4-dimethylamino benzoate [EDB]/Compound 1/HDDA

b) Compound A/Compound 1/HDDA

c) Compound A/Compound 2/HDDA

Results

Percentage transmittance at 810 cm^{-1}

No. of UV passes	0	2	4	6
a	7.79	61.74	63.42	60.97
b	13.06	60.24	65.63	60.23
c	12.48	53.43	59.83	70.15

It will be seen that the novel PEG-substituted initiators and curing agents provide good rates of reaction and high degrees of polymerisation, in addition to the good or excellent self-migration properties, shown by the other tests.

The use of novel photoinitiators of the type of compounds 1 to 3 can be expected to offer certain further advantages. Firstly, the use of PEG can be expected to have a plasticizing effect, useful to increase the flexibility, and hence the durability, of films. Secondly, the incorporation of PEG may be expected to increase the compatibility of the polymers, with paper surfaces. When polymer films cured using the novel photoinitiators are used in conjunction with paper, the extra adherence is desirable. Thirdly, PEG compounds are likely to be highly soluble in water, such that the amine curing agents could be used in conjunction with aqueous

curing formulations. These advantages are likely to be furthered, when the novel PEG-modified amine curing agents are also used.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

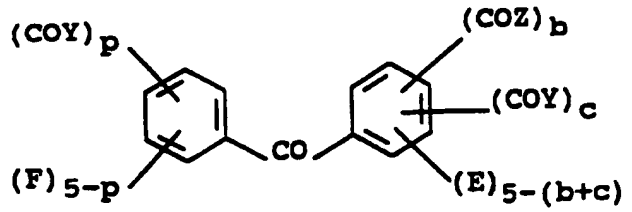
All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A benzophenone compound of the general formula



(I)

wherein:

each Z independently represents an alkylene polyol moiety or a polyalkylene polyol moiety, wherein hydroxyl groups of the polyol moiety are optionally alkylated;

each Y independently represents an alkylene polyol moiety or a polyalkylene polyol moiety, wherein hydroxyl groups of the polyol moiety are optionally alkylated; or an alkoxy group;

each E is independently selected from hydrogen or halogen atoms and alkyl, acyl, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl, alkylsulphonyl, sulphonate, amido, alkylamido, alkoxycarbonyl, halocarbonyl and haloalkyl groups;

each F is independently selected from hydrogen or halogen atoms and alkyl, acyl, nitro, cyano, alkoxy, hydroxy, amino, alkylamino, sulphinyl, alkylsulphinyl, sulphonyl, alkylsulphonyl, sulphonate, amido, alkylamido, alkoxycarbonyl, halocarbonyl and haloalkyl groups;

b represents 1 to 5;

c represents 0 to 4; and

p represents 0 to 5.

2. A compound according to claim 1, wherein

b represents 1 or 2;

c represents 0 or 1;

p represents 0 or 1;
each E represents a hydrogen atom; and
each F represents a hydrogen atom.

3. A compound according to claim 1 or claim 2, wherein one or each group Z represents a polyol moiety which is end-capped by an alkyl group.

4. A compound according to any preceding claim, wherein one or each group Z is of the general formula

$$-O-(CH_2-CH_2-O)_e-alkyl$$

where e has a mean value of from 2 to 20 and the alkyl group is a C_{1-4} alkyl group.

5. A compound according to any preceding claim, wherein one or each group Y represents a polyol moiety which is end-capped by an alkyl group.

6. A compound according to any preceding claim, wherein one or each group Y is of the general formula

$$-O-(CH_2-CH_2-O)_e-alkyl$$

where e has a mean value of from 2 to 20 and the alkyl group is a C_{1-4} alkyl group.

7. A process for the preparation of a compound of general formula I as described in any of claims 1 to 6 which comprises the esterification or transesterification of a precursor benzophenone compound to the compound of general formula I, with an appropriate optionally alkylated polyol compound having at least one hydroxyl group.

8. A polymer curing composition comprising a compound of general formula I as described in any of claims 1 to 6, together with a curing agent with which the compound of

general formula I may react, when irradiated, to generate a polymerisation radical.

9. A polymerisable composition comprising a polymerisable material, a curing agent and a compound of general formula I as described in any of claims 1 to 6.

10. A polymeric composition derived from said polymerisable composition described in claim 9 by photo-curing.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB 96/00911

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C69/78 C08F2/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 4294 Derwent Publications Ltd., London, GB; AN 94-338316 XP002009175 "photoinitiator composition and photo-curable coating composition" & JP,A,06 263 814 (TOYO INK MFG CO) , 20 September 1994 cited in the application see abstract --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

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Date of the actual completion of the international search	Date of mailing of the international search report
24 July 1996	16. 08. 96

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INTERNATIONAL SEARCH REPORT

In tional Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 4294 Derwent Publications Ltd., London, GB; AN 94-338314 XP002009176 "copolymerizable photoinitiator composition and photo-curable coating composition" & JP,A,06 263 812 (TOYO INK MFG CO) , 20 September 1994 see abstract	1-10
X	US,A,4 338 171 (BARIE, JR. ET AL.) 6 July 1982 see column 3, line 16 - line 66 see claims 1-8	1-10
X	US,A,4 602 097 (CURTIS) 22 July 1986 see examples 13-15,17 see claims 1-16	1-10

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 96/00911

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4338171	06-07-82	NONE	
US-A-4602097	22-07-86	NONE	